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Effect of particle size of mineral fillers on polymer-matrix composite shielding materials against ionizing electromagnetic radiation

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Abstract Filler particle size is an important particle that effects radiation attenuation performance of a composite shielding material but the effects of it have not been exploited so far. In this study, two mineral (hematite–ilmenite) with different particle sizes were used as fillers in a polymer-matrix composite and effects of particle size on shielding performance was investigated within a widerange of radiation energy (0–2000 keV). The thermal and structural properties of the composites were also examined. The results showed that as the filler particle size decreased the shielding performance increased. The highest shielding performance reached was 23% with particle sizes being between <7 and <74 μm.

Keywords Radiation shielding · Composite shield · Filler particle size · Size effect on attenuation

Introduction

The use of different shielding materials became common by the 20th century after a recognition that ionizing radiation caused biological hazards. Gamma and X-rays have a higher penetrating ability because of electromagnetic waves (massless and chargeless) in comparison to particulate type radiation. The most widely used ionizing electromagnetic radiation (IEMR) shielding material is lead but it does have disadvantages, those being; high toxicity, heaviness and low mechanical/chemical strength. Thus designing a new shielding materials with high efficiency and preferable properties became an important challenge as usage of radiation became widespread in the modern era.

During the last decades, composites seemed to be good solution for the above problem due to possessing both filler and matrix properties. Polymer based composites are being widely studied nowadays because of their flexibility, lightness, cheapness and mechanic/chemical strength. Several metals and metal oxides are used as filler material for polymer composites to increase the low IEMR shielding performances of the polymers. There are also numerous studies being carried on natural minerals to see if they can be used as filler materials [1, 2]. The natural forms of hematite [3] and ilmenite [4] minerals with polyester matrix were studied for the first time in our previous studies and good results were obtained and reported in detailed.

There are some important parameters that affect composite properties such as filler shape, dispersion of filler and filler particle size. According to literary studies that focused on the effect of filler particle size on properties of composites, tribological behavior of composites [5], dielectric properties [6], electrochemical performance [7], thermal stability [8], conductivity [9], mechanic properties [10, 11] were the main ones. Koops' study on filler size effect on the neutron shielding properties of multiphase composites [12] reported that the shielding performance of the composite was significantly increased as filler particle size decreased. Dong and his colleagues studied the effects of WO_3 particle size (micro and nano sizes) on epoxy based composite shields using low energy gamma rays (59.6, 121.8 and 344.1 keV). They found that linear attenuation coefficients of the composites were increased as the filler particle size decreased [13]. In another study, filler size (micro sizes) effect on lead oxide-epoxy

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composites were investigated and it was reported that size effect was negligible on mass attenuation coefficients of the composites [14]. Azman and his collegues studied filler particle size effect on X-ray transmission properties of tungsten oxide-epoxy composites. They reported that nano sized WO_3 had better attenuation properties than micro sized ones in lower tube voltages (25–35 kV) but at higher X-ray tube voltages (40–120 kV) the effect was negligible [15].

A known phenomenon is that composite filler particle size effects radiation attenuation performance of the composite materials, additionally physical and chemical properties [13] in a comprehensive survey revealed that the potential effect of filer particle size on ionizing radiation attenuation properties have not been exploited. Thus in this study, the particle size effect on hematite and ilmenite filled IEMR shielding composite properties was investigated using four different mineral filler particle sized between <7 and 74 μm. The shielding properties of the composites were also investigated in three different IEMR energy regions low (0–500 keV), intermediate (500–1000 keV) and high (>1000 keV). Any study of particle size effects in three different energy regions has not been previously encountered in the literature whereas interaction mechanisms of IEMR with matter differs mainly according to IEMR energy [16].

Experimental

Preparation of the composites

Polymers are suitable matrix materials for IEMR shielding applications because they are light, cheap and containing a large number of hydrogen that generate many interaction points for IEMR. They have lack the ability for secondary radiation due to the lack of heavier atoms in the chains. On the other hand since it lacks heavier atoms their IEMR attenuation ability is low and they have to be filled with heavy materials to prepare as an useful shield. In this study, isophytalic unsaturated polyester (PES) with a density of 1.15 g cm^{-3} was used as the matrix polymer and was reinforced with minerals.

PES was procured commercially as a PES resin in styrene monomer. The trigonal crystal structured hematite with a density of 5.26 g cm^{-3} and hexagonal crystal structured ilmenite with density of 4.72 g cm^{-3} were procured commercially in the form of natural middle sized stones. The exact content of the minerals and properties of the composite were reported in detail previously [3, 4]. The minerals were crushed by using an axial ball mill, filtered to four different sizes (<74, <50, <37, and <7 μm) with a jigging screen, homogenized and oven dried to constant weight.

Preparation of the composites was accomplished by using free radical polymerization of the PES resin after dispersing filler particles within the prepolymer as it has been reported in detail [3, 4]. Composites were prepared so as to allow 50% filler loading for each of the four different particle sizes that showed maximum IEMR shielding performance in the previous studies [3, 4].

Shielding performance measurements of the composites

The effect of filler particle size on IEMR shielding performances of the composites was investigated via gamma spectrometric system with a 110 cm^3 HPGe detector and 3.78 keV resolution at 1.33 MeV of ^{60}Co. The performance was measured at 60, 88, 122, 166, 392, 662, 898, 1173, 1333, 1836 keV gamma energies by using mixed point gamma-source containing ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{113}Sn, ^{137}Cs, ^{88}Y and ^{60}Co radionuclides. The mixed radionuclide content of the gamma-source allowed a full evaluation of the results from low (60 keV) to high (1836 keV) IEMR energy regions. Linear (μ_L) attenuation coefficients of the composites and pure lead (for comparison) was calculated after evaluation had been acquired using gamma spectra. The details from the shielding performance measurements and calculation procedures were already reported [3, 4].

Morphological-structural characterization of the composites

Fourier transform infrared spectroscopy method (FTIR-Thermo Scientific-Nicolet-1510) was used in order to understand potential effect of filler particle size on binding behavior and the nature of the interaction between filler particles and matrix. The potential effect of filler particle size on dispersability of mineral fillers with polyester matrix was investigated by using an optical microscope (BEL Photonis-MTM-1A). Then, a scanning electron microscope (SEM-JEOL-JSM-7600F) examination was performed for both fractured and polished surfaces of the composites that shows higher performance (<7 μm filler particle size) and dispersibility of the particles with polymer matrix, microstructure of the composites, and binding behavior between the filler particles and polymer matrix were examined.

Thermal characterization of the composites

Thermogravimetric analysis (Perkin Elmer-TGA4000) and differential scanning calorimetry (Perkin Elmer-DSC8000) methods were used for the thermal characterization of the composites. TGA analyses was performed for a temperature ranging from 30 to 700 °C with increment of 10 °C

Table 1 Experimentally determined μ_L (cm^{-1}) values of the composites and pure lead

IEMR energy (keV)	Shielding material								
	Pure lead	PES+ <74 μm hematite	PES+ <50 μm hematite	PES+ <37 μm hematite	PES+ <7 μm hematite	PES+ <74 μm ilmenite	PES+ <50 μm ilmenite	PES+ <37 μm ilmenite	PES+ <7 μm ilmenite
60	10.16	0.95	1.05	1.12	1.17	0.78	0.73	0.76	0.82
88	4.05	0.35	0.66	0.63	0.74	0.45	0.38	0.33	0.46
122	9.09	0.29	0.49	0.48	0.45	0.44	0.32	0.37	0.47
166	8.51	0.35	0.50	0.48	0.41	0.34	0.41	0.44	0.43
392	2.62	0.22	0.35	0.31	0.23	0.19	0.17	0.25	0.25
662	1.13	0.15	0.18	0.18	0.19	0.17	0.19	0.19	0.21
898	0.78	0.07	0.13	0.11	0.15	0.12	0.15	0.14	0.18
1173	0.63	0.15	0.13	0.18	0.16	0.14	0.14	0.18	0.17
1333	0.60	0.11	0.11	0.13	0.15	0.12	0.10	0.11	0.12
1836	0.51	0.06	0.06	0.06	0.10	0.09	0.09	0.10	0.11

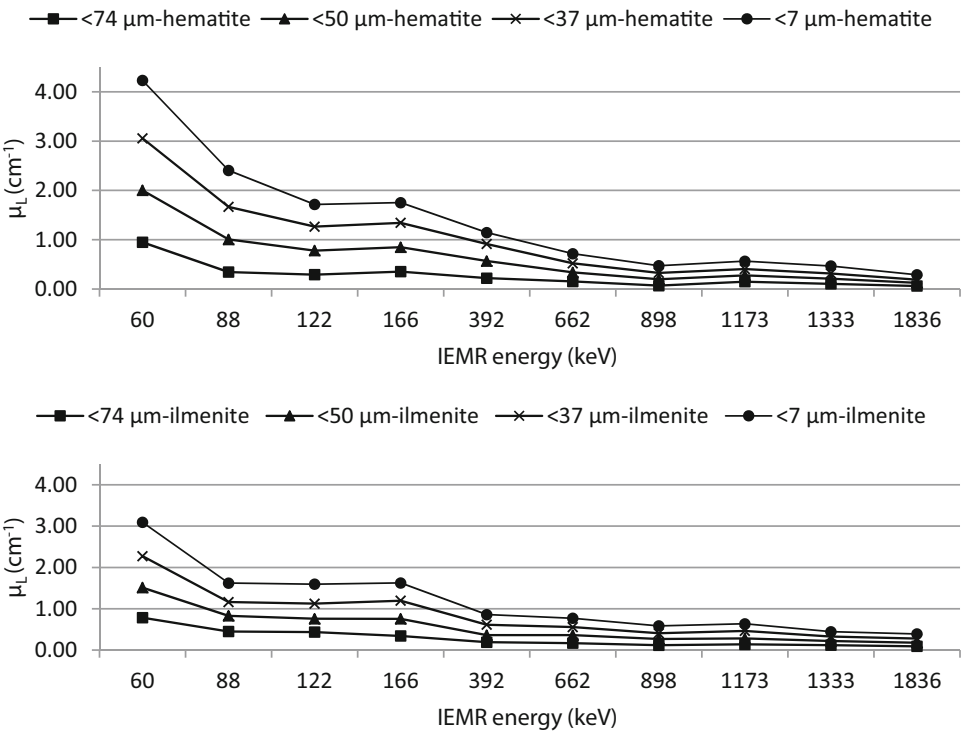

Fig. 1 Change μ_L values of the composites prepared with different filler particle sizes with IEMR energy

min^{-1} at nitrogen atmosphere and mass changes of the composites were recorded as a function of time. Information about thermal stability and composition of the composite materials, thermal stability of possibly formed byproducts, residue composition and transition temperatures of the composite materials was examined by using recorded thermograms. DSC analysis were also performed for 30−400 °C temperature range with increment of 10 °C min^{-1} and possible microcrystal formations, thermal transformations as melting point and glass transition temperatures were examined by using heat flow difference between reference matter and composites.

Results and discussion

Effect of filler particle size on shielding performance

A shielding material should reduces electromagnetic radiation's intensity according to the Bragg law as it passes

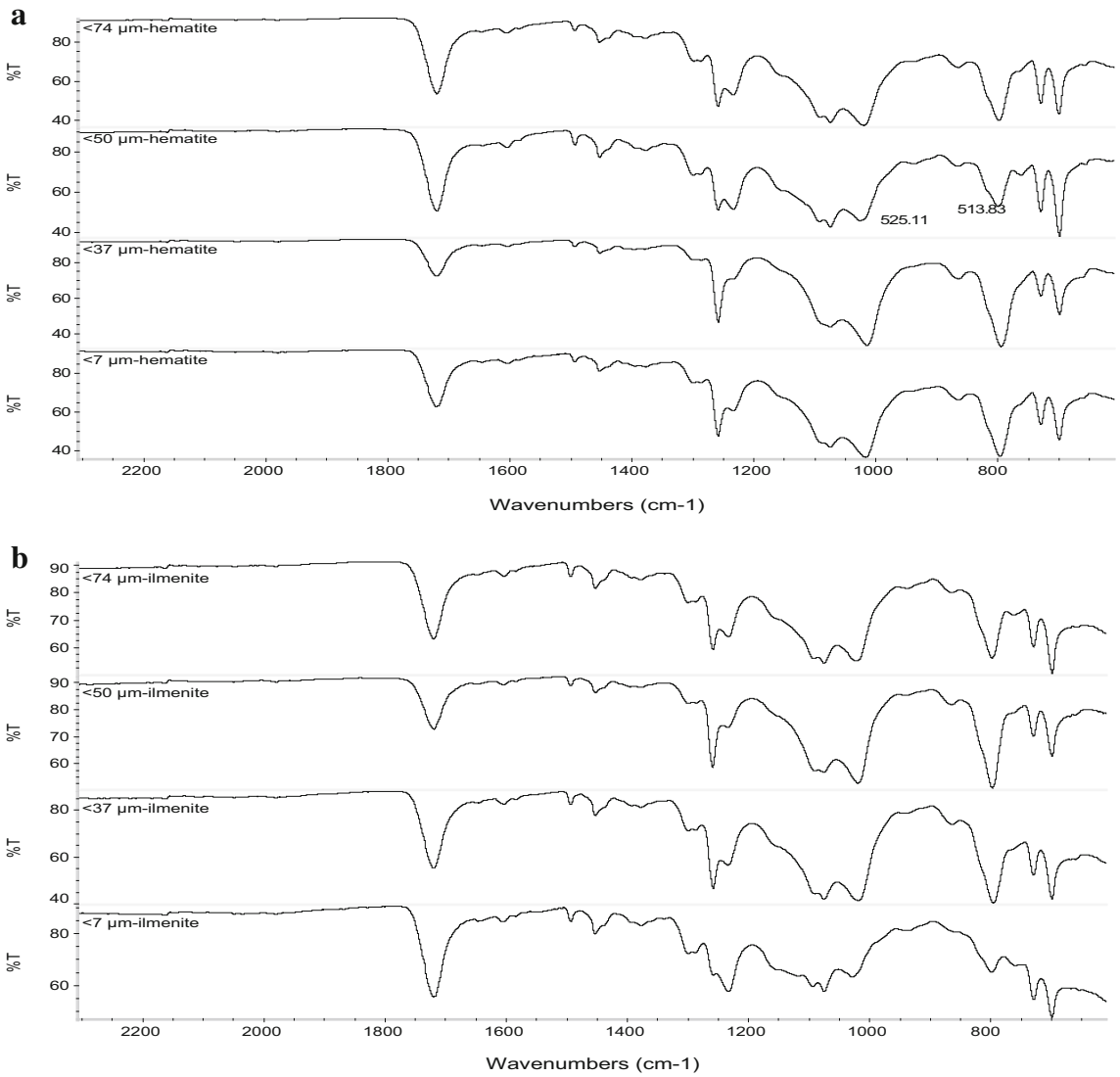

Fig. 2 FTIR spectra of hematite filled (**a**) and ilmenite (**b**) filled composites for different filler particle sizes

through the material [3]. Thus μ_L value of a material mainly describes radiation attenuation capacity per unit thickness. A larger μ_L value material enlarges this reduction, which means it has a better radiation attenuation performance. In this study the μ_L values of the composites prepared with different filler particle sizes and pure lead were calculated after the gamma spectrometric measurements [17]. Additionally, the experimentally determined linear attenuation coefficients (μ_L) of pure lead and produced composite materials at different IEMR energies are given in Table 1.

The results (Table 1) indicate that pure lead which is the most widely used shielding material has significant higher μ_L value than the composites. This was an expected results because lead is an excellent shielding material due to its high density and close packed crystal structure. On the other hand the polymeric composites had lower μ_L values due to their light weight and loose structure. The hematite ($\sim$5.26 g cm^{-3}) filled composites had higher μ_L values than ilmenite ($\sim$4.72 g cm^{-3}) filled composites due to its higher density. The interaction mechanism of IEMR with matter at different IEMR energies is related to the atomic number (related to density) of the shielding material. The predominant interaction process is photoelectric effect that is proportional to Z^5 where 'Z' represents atomic number of the target material for the IEMR energies approximately between 0 and 500 keV. On the other hand Compton effect and pair production interactions are predominant interaction for the IEMR energies approximately between 500 and 1020 keV and >1020 keV IEMR energies and are proportional to Z and Z^2, respectively [3, 4]. Thus as a result of this phenomenon when the IEMR energy increased the IEMR attenuation performances of the composites decreased sharply first but as the IEMR energy increases

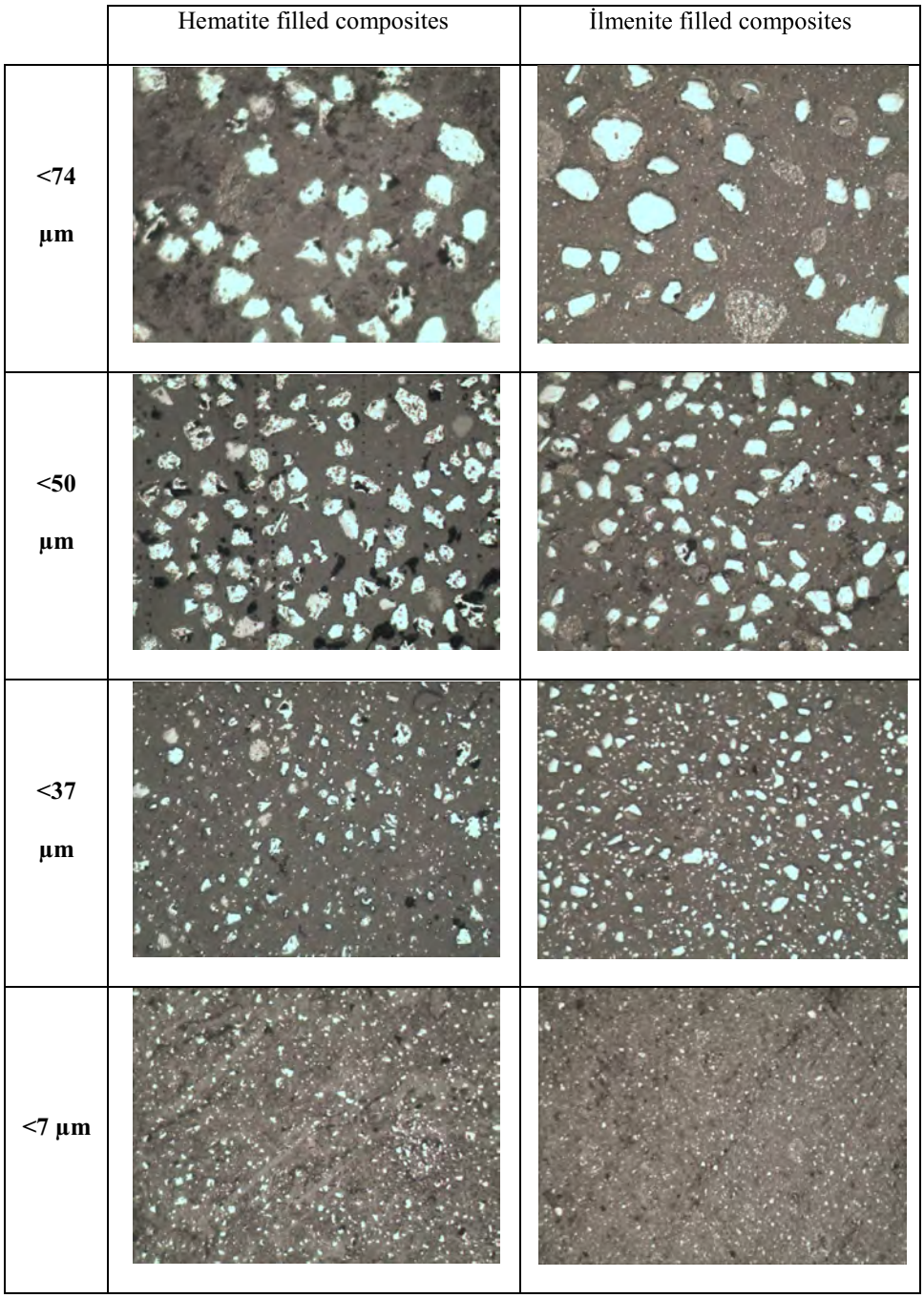

Fig. 3 Optical microscope micrographs of hematite and ilmenite filled composites for different filler particle sizes

the performance lowering became insignificant. The same behaviors of the μ_L values were also observed in the previous studies [3, 4, 18].

The determined μ_L values also showed that as the particle size of the filler mineral decreased İEMR shielding performance of the composites increased. The results are plotted against IEMR energy to emphasize this behavior clearly, Fig. 1.

The increment in μ_L values was significant at low IEMR energies and became insignificant as IEMR energies became higher. This was an expected result because low-sized particles dispersed in the polyester more continuously and the volume of the voids, that are devoid of filler particles, has decreased. These void bodies permitted electromagnetic waves to pass through with less interaction which decreases attenuation performance of the composite. Thus the effect occurs due to the packing factor (the geometry) as a result of the arrangement of the particles even though there was no change in the intrinsic attenuation properties of the elements.

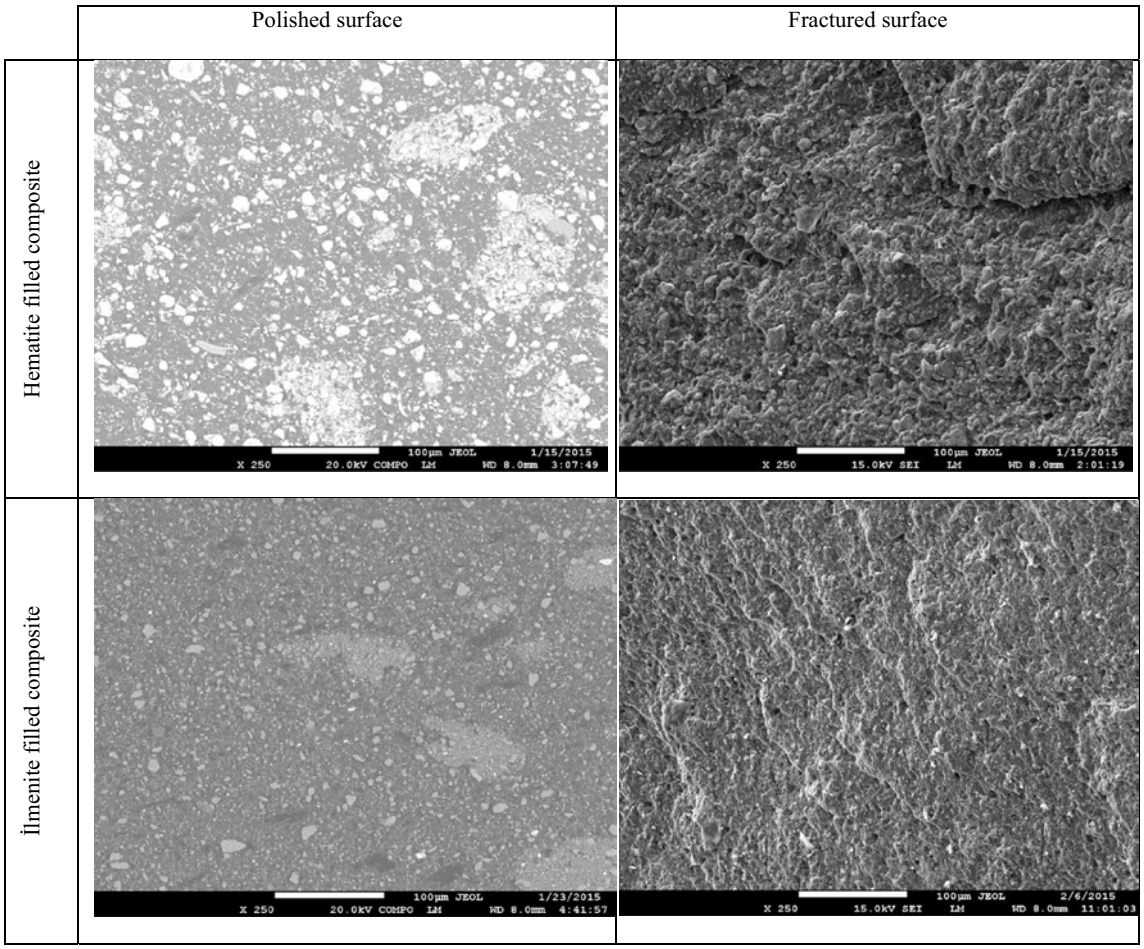

Fig. 4 SEM micrographs of hematite and ilmenite filled composites for <7 μm filler particle sizes (×250)

Effect of filler particle size on morphology-structure

The FTIR spectra of the hematite filled and ilmenite filed composites are given in Fig. 2a, b, respectively. The absorption bands corresponding to the C=O bonds at 1719 cm^{-1} [18] are seen in all types of the composites' spectra which were by using different filler particle sizes.

The FTIR spectra of different particle sized composites were in agreement with each other for both hematite filled and ilmenite filled composites. Thus there was not a meaningful difference between functional group intensities of the composites and filler particle size and it did not affect the interaction between PES matrix and mineral fillers. Also another implication of the FTIR spectra was that there was physical interaction between filler particles and polymer matrix since the absorption bands observed were similar with those belongs to polyester.

The micrographs were determined by using optical microscope studies for the hematite and ilmenite filled composites which were prepared by using different particle sized fillers as shown in Fig. 3.

Figure 3 indicates that all type of the particles dispersed homogeneously within the matrix but the lower size filler particles dispersed more closely. Thus, as the filler particle size increased the matrix areas devoid of filler increased (Fig. 3) that permitted electromagnetic waves to pass through with less interaction. Thus as the particle size of the filler increased, radiation attenuation performance of the composites decreased as it is shown in our results.

After optic microscope, the composites that showed the best attenuation performances (<7 μm) were examined by SEM in more detailed. SEM micrographs are given in Fig. 4.

The homogeneous dispersion of the filler particles within the matrix can also be seen in Fig. 4 for both hematite and ilmenite filled composites. Several coagulated filler particles were observed in the polished surface micrographs as it was expected since the decreasing filler particle size leads to filler coagulation. At the fractured surfaces of the composites filler particle holes were not observed, which means the adhesion between filler

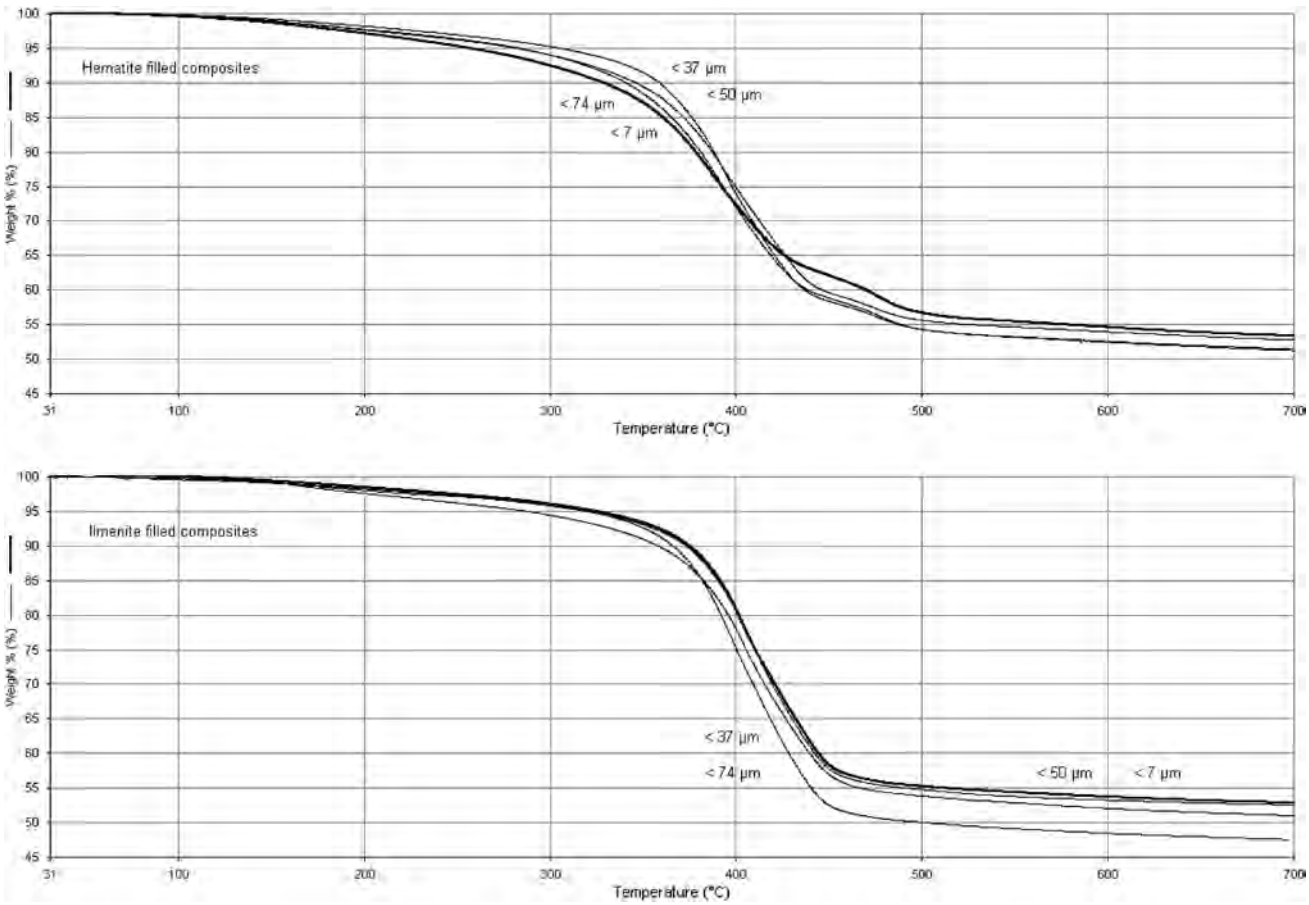

Fig. 5 TGA thermograms of the hematite and ilmenite filled composites prepared by using different filler particle sizes

particles and polymer matrix was good [19], even though surface treatment of the filler particles were at the level of production process.

Effect of filler particle size on thermal properties

The TGA thermograms of the composites prepared by using different filler particle sizes are shown in Fig. 5 for hematite and ilmenite filled composites, respectively.

The thermograms of the composites did not showed any meaningful difference from each other as it can be seen in Fig. 4. The similar thermal characteristics of the composites indicated that the filler particle size does not affect thermal characteristic of a composite significantly. The hematite filled composites showed a two step decomposition property because of the impurities that had low thermal stabilities' like SO_2 and K_2O.

In Table 2 the mass alterations of the composites, fillers and matrix for 100 °C temperature increment are given for a detailed discussion of the thermal properties.

The 86% mass loss that the composites suffer come from polyester's decomposition and approximately 14% of the polyester remained in the sample pan because no oxidative decomposition occurs to the sample in the nitrogen environment. The remaining mass loss originates from impurity contents of the natural fillers. There is also another implication from the thermal characterization and, that is the composites only decomposed <0.5% up until 100 °C, the decomposition started once the temperature was above 100 °C and above 300 °C a rapid decomposition occured. Thus the composite operating temperature was determined to be 100 °C and, that is suitable for a radiation shield when the usual operating-working conditions (generally room temperature) are considered.

The DSC analysis was also done for the composites but since the matrix polymer was a thermoset polymer any thermal transformation like melting point or glass transition was observed as expected. Thus it was understood that filler particle size does not affect thermal character of the thermoset polymer matrix.

Table 2 Mass alterations of the composites, fillers and matrix for 100 °C temperature increment

Consistuent	100 °C remaining mass (%)	200 °C remaining mass (%)	300 °C remaining mass (%)	400 °C remaining mass (%)	500 °C remaining mass (%)	600 °C remaining mass (%)	700 °C remaining mass (%)
<74 μm hematite + polyester	99.83	97.72	94.00	71.90	54.31	52.47	51.25
<50 μm hematite + polyester	99.66	97.61	94.02	74.73	55.62	53.95	52.78
<37 μm hematite + polyester	99.83	98.19	95.22	73.84	54.30	52.58	51.46
<7 μm hematite + polyester	99.58	97.10	92.45	72.32	56.68	54.60	53.37
<74 μm ilmenite + polyester	99.60	98.04	96.02	75.11	50.03	48.45	47.56
<50 μm ilmenite + polyester	100.03	98.46	96.05	80.79	55.23	53.69	52.83
<37 μm ilmenite + polyester	99.97	97.62	94.45	78.00	53.85	52.07	51.02
<7 μm ilmenite + polyester	99.77	98.27	95.82	80.33	54.79	53.27	52.52
Hematite	100.11	99.31	97.54	96.55	95.97	94.95	94.13
Ilmenite	99.61	98.89	98.06	96.86	95.68	95.13	94.76
Polyester	99.65	93.62	85.79	48.89	9.78	8.27	6.83

Conclusions

Natural hematite and ilmenite reinforced polyester which were based around a non-toxic IEMR shielding composites were prepared by using different filler particle sizes ranging from 74 to 7 μm. The FTIR analysis of the composites showed that there is not a meaningful difference between functional group intensities of the composites. Thus filler particle size does not affect interaction type between PES matrix and mineral fillers. Similarly, thermal character of the composites that were investigated by TGA and DSC studies indicated that the filler particle size did not affect thermal character of the composites significantly. Optical microscope and SEM studies confirmed that all different types of the particles dispersed homogeneously within the matrix but the lower size filler particles were seen to disperse more closely and continuously, which led to a higher IEMR attenuation performance. The attenuation performance increment that was caused by filler particle size increment ranging from <7 to 74 μm reached approximately 23%.

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